

ART. VII.—*An Occurrence of Ammonium Chloride at Frankston.*

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In the immediate neighbourhood of the Sports Oval at Frankston there was, until some two years ago, a small, shallow lake, with an island about forty yards in diameter in the centre. The lake has gradually drained, and, except after heavy rain, a dry, firm annular bed of earthy material surrounds the one-time island. The island and the banks consist of accumulations of decaying wood, roots, and leaves, together with much siliceous earth (see analytical results below). The living vegetation consists of *Acacia*, *Melaleuca*, rushes, etc.

About the middle of March, 1915, a fire was started by some boys in the ti-tree scrub on the banks and island. Apparently the fire was soon extinguished on the surface, but it has since spread underground, and has defied the efforts of local municipal officers to put it out. The authors visited the place on May 15, and again some ten days later. During these ten days heavy rain had fallen, without greatly affecting the fire. The combustion was still active and the diameter of the unburnt central portion of the island had decreased by some six or eight yards. No flames were to be seen, but white smoke issued from a number of vents in the ground. This smoke had a very specific smell, and on the walls of the fissures and in the openings whence it escaped, there were deposited very beautiful incrustations of ammonium chloride crystals, in cubes and interlacing needles. The white colour of the smoke and its specific smell were doubtless due almost solely to fumes of this salt. As the fire spread, the surface vegetation was killed at the roots, and fell down. It was unsafe to walk over the burning areas without the support of branches of scrub.

The ash left was, for the most part, very voluminous, and varied in colour from dirty white, through pink and red, to brownish purple. In parts the ash was more compact. The bed of combustible matter was apparently several feet deep.

**Analytical Work.**

One might reasonably suspect that in the course of slow combustion, the nitrogenous constituents of the decaying plant material

would undergo chemical action with sodium chloride, the presence of which in a dried-up lake near the sea would be probable. Ammonium chloride would result, and at the temperature of the combustion would be volatilised. A number of analyses have been carried out in order to ascertain definitely the nature of the materials taking part in, or produced during, the reactions which occur. The following paragraphs summarise the results.

1. Specimens of the crystalline sublimate from one of the vents contained 99.4 per cent. pure ammonium chloride, calculated from the weight of silver chloride obtained by double decomposition with silver nitrate. The balance was probably moisture, or a trace of contaminating ash. It contained no sulphate. A natural product from Vesuvius, analysed by Klaproth, contained 99.5 per cent. ammonium chloride, and 0.5 per cent. ammonium sulphate.

2. Specimens of red ash gave the following proportions of the main constituents :—

TABLE I.

	I.	II.
Silica - - - -	85.22	86.55
Alumina - - - -	8.66	6.98
Ferrie oxide - - - -	4.52	5.33
Lime - - - -	0.55	0.26
Magnesia - - - -	0.43	0.68
Sulphur trioxide - -	trace	trace
	<hr/> 99.4	<hr/> 99.8

Alkalis were not determined quantitatively. Sodium was present in small amount, and there was a minute trace of potassium. Qualitative tests showed that manganese, zinc, cobalt, nickel, barium, strontium, chromium, carbonate and chloride were absent. The complete absence of chloride is to be noticed. It is unlikely that sodium chloride would be volatilised during combustion, and unless it were washed out of the layer by heavy rain before combustion began, it is probable that there was more than sufficient ammoniacal matter produced to convert the whole of the chloride to the ammonium salt. This possibility is supported by the fact, to be mentioned later, that the yield of ammonium chloride may be increased by addition of common salt to the combustible matter. A small amount of soluble matter could be extracted by water from the ash. It contained calcium, magnesium and sulphate. On treating the ash with boiling hydrochloric acid, chlorine was evolved. As higher oxides of manganese were absent, one is inclined to suppose

this oxidation of hydrogen chloride to be due to atmospheric oxygen, the action being catalysed in a marked manner on the surface of the very finely divided ash. The acid yielded a yellow solution containing aluminium, trivalent iron, calcium, magnesium and a little sodium. An undissolved residue of fine white powder was mainly, if not entirely, silica.

The air-dried ash retained about 6 per cent. of moisture, but much larger proportions were present in samples freshly collected. From the earths, the analyses of which are detailed in the next paragraph (3), ashes were obtained which were extracted with hot water and also with dilute nitric acid. In each of the four cases examined, chloride and sodium proved to be present. These ashes were obtained by burning in an open dish small quantities of earth and organic matter; probably under such conditions of ready combustion in an abundance of air, the action between salt and nitrogenous matter does not occur to more than a slight extent.

3. Samples of earth, with accompanying organic matter, were taken from four different places. Big decayed roots and thick leafy surfaces were rejected, so that from the point of view of vegetable matter, these samples are below the general average. The water content was, of course, very variable.

It would be absurd to claim that such samples represent fairly the composition of the heterogeneous area undergoing combustion. Nevertheless, the analyses of them are not without value in giving an idea of the nature of the area.

The samples will be referred to as A, B, C and D respectively. A was taken from just below the top layer on the island, about six feet from a smoking vent; it was more earthy than the samples from other parts. B was from the middle of the island, about eight or nine inches below a very thick, leafy surface. It contained many fine roots. C was about one foot below the surface, and was quite close to a vent. It was hot and smoking when collected, fairly free from fine roots, very moist, and contained a number of tiny white specks, probably of ammonium chloride. These three samples were all from the island. D was from the bank of the lake just under the surface layer, and six feet from a smoking vent.

The following remarks are necessary in explanation of the analytical tables:—"Moisture" is that portion of the specimens which was volatilised in an air oven at 110 deg. C. "Combustible matter" represents the portion oxidised and volatilised on heating to redness in an open platinum or silica dish. The "ash" is the residual matter. "Total nitrogen" was determined by the method of Kjeldahl, oxidation of the organic material being readily accom-

plished by sulphuric acid and potassium sulphate. By "free nitrogen" is to be understood that nitrogen which may be distilled (as ammonia or substituted ammonias) from a sample of earth by boiling with sodium hydroxide solution for one hour. It cannot be taken as giving a measure of the ammonium salts present before combustion, because even after prolonged boiling the steam distilling was found to be alkaline. Doubtless there is a progressive action between the alkali and the nitrogenous matter; to limit the time of distillation to one hour is arbitrary. The estimations of total chloride proved to be very tedious. Portions of each sample were extracted three or four times with boiling water; the resulting filtrates contained brown colloidal matter. They were evaporated to small volumes, and in one case taken completely to dryness. In this case, sodium chloride crystals separated along with the brown matter. Evaporation did not suffice to render the latter insoluble; the greater proportion again formed a colloidal suspension on the addition of water. To each extract a few drops of nitric acid were added, the solution boiled and silver nitrate added. The silver chloride formed was fine grained and yellowish owing to colloidal contamination. It could not be made to coagulate except in one case (D), where much less colloidal matter had been removed in the extraction. After settling, the supernatant liquid was decanted through a Gooch crucible, and the residue dissolved in ammonia. The deep brown colour of this solution was possibly due in part to the reduction of the ammoniacal silver complex to colloidal metal, by organic matter. On reprecipitation with excess nitric acid, the silver chloride was white and coagulable. The liquid was poured through the Gooch crucible, but on addition of water or dilute nitric acid, the precipitate turned to a milky suspension, which the asbestos layer in the crucible would not retain. Boiling again coagulated it. The liquid was decanted away, the precipitate dissolved in ammonia (the solution again being deep brown in colour), and reprecipitated with nitric acid. A repetition was necessary before a satisfactory product was obtained. In the following tables, all figures represent percentages :—

TABLE II.

	A.	B.	C.	D.		A.	B.	C.	D.
Moisture	- 35.3	- 47.8	- 47.4	- 50.4	...	Calculated on dried material.			
Ash	- 53.7	- 37.1	- 43.2	- 31.5	...	83.0	- 71.1	- 82.0	- 63.4
Combustible matter	- 11.0	- 15.1	- 9.5	- 18.2	...	17.0	- 28.9	- 18.0	- 36.6

All subsequent figures are percentages calculated upon dried material.

TABLE III.

	Total Nitrogen.				Free Nitrogen.			
	A.	B.	C.	D.	A.	B.	C.	D.
Calculated as								
Nitrogen	- 0.47	- 0.84	- 0.79	- 1.14 ...	0.07	- 0.10	- 0.16	- 0.13
Ammonia	- 0.57	- 1.02	- 0.96	- 1.39 ...	0.08	- 0.12	- 0.20	- 0.16
Ammonium chloride	- 1.80	- 3.19	- 3.00	- 4.37 ...	0.26	- 0.37	- 0.62	- 0.51

TABLE IV.

	A.	B.	C.	D.
Chloride, calculated as				
Chlorine	- 0.44	- 0.64	- 0.36	- 0.22
Sodium chloride	- 0.72	- 1.06	- 0.59	- 0.36
Ammonium chloride	- 0.66	- 0.97	- 0.54	- 0.33

### Production of Ammonium Chloride.

Some experiments were carried out with a view to ascertaining the yield of ammonium chloride from slow combustion of sample B. It was not, of course, possible to reproduce the conditions prevailing at Frankston.

A short, hard glass tube was filled with material. Owing to difficulty in absorbing the products from large amounts, it was necessary to work with only five grammes at a time. The sample, heated from the outside, was slowly burnt in a current of air. The current carried the products of combustion through a long tube in which were spaced twelve wet glass-wool plugs, and then through a bubbler containing water. All visible smoke or fume was removed before the last plug was reached. Care was taken to make the combustion complete, and to prevent condensation of products in the hard glass tube. The plugs in the long tube were pushed together, and washed with hot distilled water until free from chloride. The washings, together with the water from the bubbler, were made alkaline with potassium hydroxide free from chloride, and evaporated to dryness. The residue was very gently ignited, the solution then acidified with nitric acid, filtered and precipitated with silver nitrate. The silver chloride was weighed in a Gooch crucible. Calculating the chloride as ammonium chloride, the amount of the latter obtained was equal to 0.092 per cent. of

the quantity of (dried) B taken. When 10 per cent. of sodium chloride was mixed with the earth sample before analysis, the yield was increased to 0.29 per cent. These figures must not be given too much weight, for the amounts of material dealt with were small, and it is possible that traces of sodium chloride may have been volatilised during the combustion. In any case, the amount of ammonium chloride produced must depend very largely upon the conditions of the combustion, such as air supply, temperature, time, and so on. The attempt to reproduce artificially the natural combustion is, of course, difficult, and the result is inevitably unsatisfactory.

### Conclusion.

In most, if not all, places where ammonium chloride occurs naturally, there is present vegetable matter in a more or less advanced state of decay, together with chlorides. The production of ammonium chloride is greatly accelerated by heating, and the occurrences near volcanoes such as Etna, Stromboli, Vesuvius, and others are greatest where lava spreads over soil and vegetation.

Abegg (*Hdb. anorg. Chem.*, III., 3, p. 250) states that in Egypt, where ammonium chloride is obtained from the soot from burnt camel dung, ammonia is probably formed by processes of decay in the dung before burning. This, however, is most likely not so in the other case cited by Abegg, where ammonium chloride is produced by burning a mixture of coal, salt, animal offal and clay. Probably here the first stage is the destructive distillation by heat of the organic matter, with the production of ammonia or simple ammoniacal compounds. Reaction occurs between these and the metallic chlorides. There is every reason to suppose that this is what is happening in the Frankston deposit. One may suppose that there is a considerable supply along the seashore of the material necessary for such a formation of ammonium chloride.

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